

PTO 04-1326

CY=JA DATE=19800709 KIND=A
PN=55-090684

PRODUCTION OF SOFT ARTIFICIAL LEATHER
[Junan na jinko hikaku]

Sadahiko Yasui, et al.

UNITED STATES PATENT AND TRADEMARK OFFICE
Washington, D.C. January 2004

Translated by: FLS, Inc.

PUBLICATION COUNTRY	(19): JP
DOCUMENT NUMBER	(11): 55090684
DOCUMENT KIND	(12): A
PUBLICATION DATE	(43): 19800709
PUBLICATION DATE	(45):
APPLICATION NUMBER	(21): 53158632
APPLICATION DATE	(22): 19781225
ADDITION TO	(61):
INTERNATIONAL CLASSIFICATION	(51): D06N 3/00
DOMESTIC CLASSIFICATION	(52):
PRIORITY COUNTRY	(33):
PRIORITY NUMBER	(31):
PRIORITY DATE	(32):
INVENTOR	(72): YASUI, SADAHIKO; ISHIKAWA, TAKEO; SHIMA, TSUKASA; NAKAMAE, KENJI
APPLICANT	(71): ASAHI CHEMICAL INDUSTRY CO., LTD.
TITLE	(54): PRODUCTION OF SOFT ARTIFICIAL LEATHER
FOREIGN TITLE	[54A]: JUNAN NA JINKO HIKAKU

1. Title of the Invention

Production of Soft Artificial Leather

2. Claims

1. Production of soft artificial leather, characterized by packing an elastic polymer into the voids in an unwoven fabric or unwoven fabric-shaped compound sheet produced by spraying a high-speed water stream into and confounding the constituent fibers of a compound sheet obtained by laminating a knit or weave onto an unwoven web containing a 20:80 to 80:20 ratio by weight mixture of 0.5 denier or less extremely fine short fibers and polyvinyl alcohol short fibers that are insoluble in cold water but soluble in hot water, or onto the back or an inner layer of said unwoven web, then dissolving and removing said polyvinyl alcohol short fibers by hot water.

2. Production of soft artificial leather described in Claim 1, wherein the above-mentioned unwoven web is produced by paper-making.

3. Production of soft artificial leather described in Claim 2, wherein the above-mentioned extremely fine short fibers are 2 to 15 mm in length, and the above-mentioned polyvinyl alcohol short fibers that are insoluble in cold water but soluble in hot water are 0.5 to 10 deniers in density and 2 to 15 mm in length.

*Numbers in the margin indicate pagination in the foreign text.

4. Production of soft artificial leather described in Claim 1, wherein the above-mentioned unwoven fabric-shaped compound sheet is produced from a compound sheet formed by laminating a knit or weave of 10 to 150 g/m² weight onto the back of an unwoven web of 50 to 200 g/m² weight, and the total weight of above-mentioned extremely fine short fibers and the above-mentioned knit or weave in this unwoven fabric-shaped compound sheet is 80 to 200 g/m² weight.

5. Production of soft artificial leather described in Claim 1, wherein the above-mentioned unwoven fabric-shaped compound sheet is produced from a compound sheet formed by laminating two unwoven webs of 50 to 150 g/m² weight and a knit or weave of 10 to 100 g/m² weight with the knit or weave as the middle layer.

6. Production of soft artificial leather described in Claim 5, wherein one of the above-mentioned two unwoven webs is a 100:0 to 40:60 ratio mixture and the other is a 60:40 to 0:100 ratio mixture of the above-mentioned extremely fine short fibers and the above-mentioned polyvinyl alcohol short fibers that are insoluble in cold /514 water but soluble in hot water.

7. Production of soft artificial leather described in Claim 1, wherein the above-mentioned high-speed water stream is a columnar rectilinear stream sprayed from a 0.005 to 0.3 mm diameter nozzle under 5 to 35 kg/cm² pressure.

8. Production of soft artificial leather described in Claim 1, wherein the above-mentioned elastic polymer is a polyurethane

elastomer.

9. Production of soft artificial leather described in Claim 1, wherein the packed weight of the above-mentioned elastic polymer is 50% to 100 wt% of the total weight of the above-mentioned extremely fine short fibers and the above-mentioned knit or weave.

10. Production of unwoven fabric or unwoven fabric-shaped compound sheet, characterized by spraying a high-speed water stream into and confounding the constituent fibers of a compound sheet formed by laminating a knit or weave onto an unwoven web containing a 20:80 to 80:20 ratio by weight mixture of the above-mentioned extremely fine short fibers and the above-mentioned polyvinyl alcohol short fibers that are insoluble in cold water but soluble in hot water, or onto the back or an inner layer of said unwoven web.

3. Detailed Explanation of the Invention

This invention pertains to production of soft artificial leather. Artificial leather is produced by packing an elastic polymer into the voids in a confounded unwoven fabric. It is known that the finer the constituent fibers of the unwoven fabric, the softer and more supple the feel of the artificial leather. Furthermore, it is well-known that using 0.5 denier or less extremely fine fibers is essential to produce artificial leather with a downy nap like suede. However, unwoven fabric is generally confound by a needle punch, and since a needle punch moves and confounds fibers by catching the fibers on the barb of the needle, extremely fine fibers with little

tension are easily cut and difficult to confound well. Therefore, an unwoven fabric of extremely fine fibers can only be produced by a special method such as the island fiber method. However, a technique for confounding unwoven fabric by spraying a high-speed water stream is being developed. This technique makes it possible to handle 0.5 denier or less extremely fine fibers, and several methods have been offered for producing suede-like artificial leather by this method. According to these methods, an unwoven fabric-shaped compound sheet can be produced by confounding together the fibers of an unwoven fabric and a knit or weave. This can produce a two-layer laminate of an unwoven fabric and a knit or weave or a three-layer laminate having a knit or weave between two layers of an unwoven fabric, and can solve the poor dimensional stability and inadequate strength that are the drawbacks of unwoven fabrics. The present invention seeks to produce a soft artificial leather using the confounding technique of spraying a high-speed water stream with characteristics such as described above into an unwoven fabric or unwoven fabric-shaped compound sheet.

Unwoven fabrics or unwoven fabric-shaped compound sheets produced by a high-speed water stream using extremely fine fibers tend to have high apparent density due to the effect of pressurizing the high-speed water stream to assure that the fibers are fine. When an artificial leather is produced by packing an elastic polymer into such an unwoven fabric or unwoven fabric-shaped compound sheet, the

elastic polymer does not pack well, or if the elastic polymer can well packed, the elasticity of the elastic polymer cannot be realized due to the high apparent density of the unwoven fabric or unwoven fabric-shaped compound sheet, and the artificial leather ends up feeling like paper. The present inventors extensively studied methods for producing an unwoven fabric or unwoven fabric-shaped compound sheet of a suitable apparent density of 0.08 to 0.25, and preferably 0.10 to 0.20, for producing artificial leather with a soft and supple feel for the reasons stated above, from 0.5 denier or less extremely fine fibers using the confounding method of spraying a high-speed water stream. In Japan Patent Application No. 52-89148, the present inventors offered a method for producing an unwoven fiber base using extremely fine short fibers A and short fibers B, producing an artificial leather from this, then removing short fibers B as a method for producing a soft artificial leather sheet. They found that this method was the most suitable for the above purpose, and after further study, achieved the present invention. Specifically, this invention pertains to production of soft artificial leather characterized by packing an elastic polymer into the voids in an unwoven fabric or unwoven fabric-shaped compound sheet produced by spraying a high-speed water stream into and confounding the constituent fibers of a compound sheet obtained by laminating a knit or weave onto an unwoven web containing 20:80 to 80:20 ratio by weight a mixture of 0.5 denier or less extremely fine short fibers

and polyvinyl alcohol short fibers that are insoluble in cold water but soluble in hot water, or onto the back or an inner layer of said unwoven web, then dissolving and removing said polyvinyl alcohol short fibers by hot water.

Because it is extremely soft, artificial leather produced by this invention is especially suited to clothing applications. /515
Although it can also be finished to a silvered surface by coating the front with a polyurethane elastomer or polyamino acid resin, it is especially ideal for making a suede-like surface by nap work using 0.5 denier or less extremely fine fibers.

It is thought that the reason why artificial leather produced by this invention is extremely soft is due to the following two effects.

Effect ①: Because an unwoven fabric or unwoven fabric-shaped compound sheet is produced by mixing extremely fine short fibers and PVA fibers and the PVA fibers are removed after packing with an elastic polymer, the vestiges left in the artificial leather where the PVA fibers were removed become voids, making the artificial leather lower density and softer.

Effect ②: Because PVA fibers that are thicker than the extremely fine short fibers are mixed in, even confounding treatment by spraying a high-speed water stream only increases the unwoven fabric or unwoven fabric-shaped compound sheet in apparent density due to the bulk retention effect of the thick PVA fibers. Therefore, it can easily be packed with an elastic polymer to produce artificial

leather with a soft leather-like feel.

Although effect ① is unaffected by the shape of the PVA fibers, effect ② differs greatly depending on the shape of the PVA fibers. Therefore, it is preferable to select PVA fibers of an ideal shape as described below.

This invention will be described in detail following its production process. First, 0.5 denier or less extremely fine short fibers are prepared. Using 0.5 denier or less extremely fine short fibers is indispensable for producing artificial leather having a soft and supple feel, and also for producing artificial leather with a fine suede texture when giving the front a suede finish. The fiber base material is not specially restricted so long as it is used in conventional artificial fibers, and polyethylene terephthalate (PET), Nylon 6, Nylon 66, polyacrylonitrile, or rayon, for example, can be used. Extremely fine fibers can be spun by conventional wet, dry, or melt spinning methods, and the extremely fine fibers of Japan Patent Application No. 53-72728, for example, can be used. Fibers spun by special spinning methods, including compound spun fibers, such as island fibers or divided fibers, can also be used. This is because these are easily mixed with the polyvinyl alcohol short fibers that are insoluble in cold water but soluble in hot water used with them, and easily confounded by spraying with a high-speed water stream. The length of the extremely fine fibers differs depending on the method for producing the unwoven web described below, and therefore is

selected according to the method for producing the unwoven web.

In addition to 0.5 denier or less extremely fine short fibers (hereafter abbreviated as "extremely fine short fibers"), polyvinyl alcohol short fibers that are insoluble in cold water but soluble in hot water (hereafter abbreviated as "PVA fibers") are used. These need not always be PVA fibers for the purpose of this invention, and any fibers may be used so long as they differ in solvent solubility from the extremely fine short fibers, allowing them to be selectively removed after packing with an elastic polymer. PVA fibers, however, are used in this invention for such advantages as they can be easily selectively removed just by heating in water and can be easily procured, being used as a base material for paper-making. The length of the PVA fibers is the same as the extremely fine short fibers, and is selected as suitable for applying to production of an unwoven web. A suitable density for PVA fibers is 0.5 to 10 deniers. Less than 0.5 denier not only complicates fiber production, but also cannot maintain a high bulk when confounding by a high-speed water stream, and there is no advantage to using less than 0.5 denier PVA fibers which are difficult to produce and only achieve half the effect of mixing in PVA fibers.

Using PVA fibers that are thicker than the extremely fine short fibers makes an unwoven fabric or unwoven fabric-shaped compound sheet that is highly bulky without being highly dense even after confounding treatment by spraying a high-speed water stream. The

extremely fine short fibers give an unwoven fabric or unwoven fabric-shaped compound sheet with a low apparent density due to distributing PVA fibers that maintain high bulk. If the PVA fibers are too thick, however, not only does the fabric become too bulky, but the extremely fine short fibers are too short relative to the voids created by the PVA fibers, and the extremely fine short fibers do not stay mixed with the PVA fibers. Therefore, the PVA fibers should be no more than 10 deniers in density, and ideally four to forty times the density of the extremely fine short fibers. Moreover, although the length of the PVA fibers is limited by the process for producing an unwoven web, the longer the fibers, the greater their high bulk retention effect.

PVA fibers are insoluble in room-temperature water, but dissolve in hot water such as 60°C or hotter water. PVA fibers are removed in this invention by hot water after packing with an elastic polymer, /516 but are able to achieve the purpose of this invention because they do not dissolve so long as they are not heated even if water is used in earlier steps.

Extremely fine short fibers and PVA fibers are changed to an unwoven fabric by a dry method such as the card cross-layer random warper method, or the paper-making method of dispersing extremely fine short fibers and PVA fibers in a solution, then collecting on a net. The paper-making method is preferred in this invention because extremely fine fibers are difficult to handle by dry methods. Since two types of short fibers are mixed to produce an unwoven fabric in

this invention, the paper-making method is also ideal in terms of mixing evenly. The length of the extremely fine short fibers and PVA fibers is limited by the production process, and 15 to 60 mm is suitable for dry methods and 2 to 15 mm is suitable for paper-making. Less than 2 mm, besides tending to let fibers drop out of the unwoven fabric or unwoven fabric-shaped compound sheet, also produces problems such as washing out during confounding treatment by spraying a high-speed water stream. Greater than 15 mm impairs dispersing in a paper-making slurry, producing an uneven unwoven web after the paper-making process. To produce an unwoven fabric mixing extremely fine short fibers and PVA fibers by paper-making, a slurry is made by evenly dispersing the two types of fibers in a solution, then the fibers may be collected by filtering through a wire screen. Water, being economical and nonpolluting, is generally used as the solution. A thickener or surface active agent such as polyacrylamide is added to improve dispersion of the extremely fine short fibers. Mixing in PVA fibers shows better effect as the extremely fine short fibers are more thoroughly dispersed. Therefore, the mixture ratio of extremely fine short fibers and PVA fibers in terms of paper-making is especially preferably 95:5 to 0:100.

A high-speed water stream is sprayed into the unwoven web obtained as described above to confound the constituent fibers and produce an unwoven fabric, but the unwoven web may be laminated with a knit or weave before this. The mode for laminating with a knit or

weave may be to laminate the unwoven web onto one side or both sides of the knit or weave, but the indispensable condition is that the unwoven fabric-shaped compound sheet confounded by spraying a high-speed water stream have at least one unwoven fabric layer. Spraying a high-speed water stream into such a laminated sheet of an unwoven web and a knit or weave confounds the fibers within the unwoven web and the fibers in the unwoven web with the knit or weave to produce a single unified unwoven fabric-shaped compound sheet. The purpose of laminating with a knit or weave is to improve the strength and dimensional stability of the unwoven fabric as described above. The knit or weave used may be a conventional knit or weave of long fibers or spun fibers, but a knit or weave of 10 to 150 g/m² weight in the case of a two-layer laminated sheet or 10 to 100 g/m² weight in the case of a three-layer laminated sheet is suitable for the purpose of this invention. Less than 10 g/m² weight is not enough to have an improving effect on the unwoven fabric, while exceeding the upper limit makes it difficult to laminate with the unwoven fabric layer, gives the artificial leather produced a knit or weave feel that is far from the feel of leather, achieves only half the effect of laminating with an unwoven fabric layer, and does not greatly differ from synthetic leather produced from a knit or weave. An "unwoven fabric-shaped compound sheet" in this invention indicates a knit or weave that has been laminated with at least one unwoven fabric layer, which is then confounded and unified by spraying a high-speed water

stream as described above.

The method for laminating the unwoven web with a knit or weave can be the method of laminating a knit or weave with an unwoven web prepared beforehand, or the method of forming an unwoven web simultaneously on top or on both sides of a knit or weave. When possible, the method of forming both parts of the laminated sheet simultaneously is more convenient.

The unwoven web or a laminated sheet of the unwoven web and a knit or weave becomes an unwoven fabric or an unwoven fabric-shaped compound sheet by spraying with a high-speed water stream to confound its constituent fibers. The method of confounding constituent fibers by spraying a high-speed water stream is the same as described in sources such as U.S. Patent No. 3,508,308 or 3,620,903. Fibers can also be confounded by a high-speed stream other than water, but using a stream of water is the most suitable for such reasons as water has great fiber confounding force, is cheap and can be easily procured, and is harmless and easy to handle. Additives such as thickeners can be added to the water or the temperature of the water can be raised, but the water temperature should not be higher than the solution temperature of the PVA fibers. The water stream can be used in a form such as a columnar rectilinear stream, a fan-shaped stream, or a sprinkled stream, but a columnar rectilinear stream is preferred for its greater fiber confounding force. The method for spraying a high-speed water stream into the unwoven web or a laminated sheet of the /517

unwoven web and a knit or weave to confound its constituent fibers will be explained in detail, taking the case of using a columnar rectilinear stream: An unwoven web or a laminated sheet of an unwoven web and a knit or weave is placed on a support with the knit or weave on the bottom in the case of a two-layer laminated sheet. This support is preferably a shape that allows sprayed water to be quickly removed, and a net shape such as a 40 to 200 mesh wire screen is ideal. A wire screen with too large a mesh becomes clogged with short fibers or lets short fibers through if the length of the fibers is too short. Drainage is preferably accelerated by suctioning from below the wire screen. Failing to remove sprayed water causes a confluence of short fibers that impairs the quality of the unwoven fabric or unwoven fabric-shaped compound sheet. This wire screen can also be used as a conveyor to facilitate confounding treatment of long fabrics. In addition, a 0.05 to 0.5 mm diameter columnar rectilinear nozzle is prepared above these, and water is sprayed toward the unwoven web or laminated sheet from this nozzle by a means such as a pump under 5 to 35 kg/cm² pressure. If the unwoven web or laminated sheet is long, several nozzles are arranged across its width and the supporting wire screen is used as a conveyor. The nozzle may be fixed or moved periodically, such as back and forth or in a circle, within a plane parallel to the supporting wire screen. Moving the nozzle can lengthen the track described by the water stream on the unwoven web or laminated sheet and increase nozzle

efficiency. A nozzle diameter within a range from 0.05 to 0.5 mm can be used, but 0.05 to 0.3 mm is especially preferred. This is because too large a nozzle diameter increases the volume of water sprayed, which tends to reduce the quality of the unwoven fabric or unwoven fabric-shaped compound sheet due to poor water drainage as described above. The water pressure must be increased the smaller the diameter of the nozzle or the faster the tracking speed of the water stream described above, but for a 0.2 mm nozzle diameter and 1 to 7 m/min track speed, for example, 5 to 20 kg/cm² is suitable if the length of the extremely fine short fibers and PVA fibers is no more than 25 mm, and 20 to 35 kg/cm² is suitable if the length is greater than 25 mm. Producing an unwoven web by paper-making using a short fiber length is also preferred in terms of facilitating confounding treatment by spraying a high-speed water stream. A suitable distance from the nozzle spray opening to the supporting wire screen is 5 to 100 mm. The force of the water stream becomes too weak if this distance is too great. The explanation above used the method of spraying a water stream from the nozzle above to the unwoven web below or toward the laminated sheet as an example, but this was only because this is the most natural method, and this invention is not limited to this method. The confounding treatment here can also be used to treat the same side repeatedly as required, or to treat from the reverse side. In the case of an unwoven fabric-shaped compound sheet having an unwoven fabric or a knit or weave as a middle layer, confounding

treatment by spraying a high-speed water stream from the reverse side is preferred.

The preferred physical properties and composition of the unwoven fabric or unwoven fabric-shaped compound sheet produced by the steps described above are 100 to 500 g/m² weight, 0.5 to 2 mm thickness, 0.15 to 0.49 g/cm³ apparent density, and 80:20 to 20:80 ratio by weight of extremely fine short fibers to PVA fibers. Although the weight and thickness may be selected to match the weight and thickness of the artificial leather to be produced, the apparent density is preferably in the range given above. A low density less than 0.15 g/cm³ is difficult to maintain in later steps, while greater than 0.49 g/cm³ does not allow enough packing of elastic polymer, making it difficult to obtain a leather-like feel. The ratio by weight of extremely fine short fibers to PVA fibers should be in the range given above. Outside of this range, too few PVA fibers is not enough to have a softening effect on the artificial leather of this invention, while too many reduces the weight of extremely fine short fibers, making it difficult for the artificial leather obtained to have what could be called a leather-like feel.

Because the PVA fibers are removed in this invention after packing an elastic polymer into the voids in the unwoven fabric or unwoven fabric-shaped compound sheet, the artificial leather is constituted of a [illegible] of extremely fine short fibers and an elastic polymer. Therefore, this point must be considered when

producing the unwoven fabric or unwoven fabric-shaped compound sheet. Indicated as the preferred ranges of the physical properties of the part of the unwoven fabric or unwoven fabric-shaped compound sheet occupied by extremely fine short fibers or extremely fine short fibers and a knit or weave (properties assuming PVA fibers have been removed from the unwoven fabric or unwoven fabric-shaped compound sheet while maintaining the same thickness), the following points, for example, should be considered:

- ① 0.08 to 0.25 g/cm³ apparent density
- ② 80 to 200 g/m² weight
- ③ at least 30 g/m² weight in the case of unwoven fabric

/518

These are the ideal ranges for producing artificial leather with a leather-like feel.

An "unwoven web" is defined in this invention as a random web of mixed and collected extremely fine short fibers and PVA fibers, but a sheet produced by an unwoven web producing apparatus may be used as an unwoven web as is, or several sheets may be laminated to form one unwoven web. Except when an unwoven web of the required weight cannot be produced in terms of production or other problems, however, it is easy to produce an unwoven web of the preferred weight. Unwoven webs with different compositions, such as the mixture ratio of extremely fine short fibers to PVA fibers, may also be laminated. The essential point is that the weight of the unwoven fabric or unwoven fabric-

shaped compound sheet produced be within the preferred range, and unwoven webs may be laminated so long as the mixture ratio of extremely fine short fibers to PVA fibers is in a range from 80:20 to 20:80. Laminating unwoven webs of different compositions to form a single unwoven fabric layer is not a very desirable method, however, because spraying a high-speed water stream can cause fibers to shift, creating spots along the track of the high-speed water stream. Since it has two unwoven fabric layers, an unwoven fabric having a knit or weave as the middle layer does not produce the problem of tending to create spots even when unwoven webs of different compositions are laminated on either side of the knit or weave. This method is especially effective for producing soft, suede-like artificial leather. Artificial leather may be softened by increasing the number of PVA fibers in the unwoven web, but producing suede-like artificial leather requires abundant extremely fine short fibers on the front, which prevents increasing the mixture ratio of PVA fibers. To solve this dilemma and produce artificial leather having a fine suede-like front, an artificial leather with many extremely fine short fibers on the front may be produced from an unwoven fabric-shaped compound sheet produced by laminating an unwoven web with a 40:60 to 100:0 mixture ratio and an unwoven web with a 0:100 to 60:40 mixture ratio of extremely fine short fibers to PVA fibers on either side of a knit or weave. Because there is a knit or weave middle layer between the two unwoven webs in this case, there is little shifting of fibers

between layers during confounding treatment by a high-speed water stream, preventing the spots that tend to occur when there are different compositions without a knit or weave in between.

Artificial leather is produced from an unwoven fabric or unwoven fabric-shaped compound sheet by packing an elastic polymer into its voids, but in this invention, a pretreatment can be applied before this. Examples of pretreatments include napping treatment, starching, and coating with sizing. Starching is a conventional method in production of artificial leather. While simultaneously facilitating handling the unwoven fabric or unwoven fabric-shaped compound sheet by starching, the sizing prevents the constituent fibers from adhering due to the elastic polymer. Napping treatment is effective when finishing artificial leather to a suede-like surface, and can simultaneously improve the surface lubrication of the unwoven fabric or unwoven fabric-shaped compound sheet when followed by buffing. Sizing is also coated when finishing to a suede-like surface. The method of applying napping treatment after packing with an elastic polymer does not give an excellent suede-like surface when producing a suede-like artificial leather from an unwoven fabric or unwoven fabric-shaped compound sheet produced by confounding treatment by spraying a high-speed water stream. Napping treatment can produce artificial leather with a satisfactory suede-like surface by coating sizing on this napped surface to prevent elastic polymer being packed onto the napped surface. Because it is to prevent the elastic polymer

from adhering wherever it is coated, the sizing for starching can be any sizing so long as it does not dissolve when packing the elastic polymer and can be removed after the elastic polymer has been packed. Because the elastic polymer is normally packed using an N,N-dimethylformamide (DMF) solution, a water-soluble sizing that does not dissolve or degrade in DMF, such as polyvinyl alcohol (PVA) sodium carboxymethylcellulose (CMC), is ideal. Napping treatment can be varied by adjusting conditions such as the length and fineness of the raised nap, and is improved by buffing with emery paper.

An elastic polymer is packed into the pretreated unwoven fabric or unwoven fabric-shaped compound sheet. "Packing an elastic polymer" means providing an elastic polymer in the voids in the unwoven fabric or unwoven fabric-shaped compound sheet. The packing method is to /519 immerse the unwoven fabric or unwoven fabric-shaped compound sheet in a solution or dispersion of an elastic polymer, impregnate the solution or dispersion of an elastic polymer into the voids in the unwoven fabric or unwoven fabric-shaped compound sheet, then remove the solution or dispersion by drying or immerse in a solution that solidifies the elastic polymer to solidify the elastic polymer. A polymer such as polyurethane elastomer (PU), SBR, or NBR is used for the elastic polymer, but PU is normally used for its excellent physical properties and the satisfactory feel it gives to artificial leather. PU is used as an aqueous solution or aqueous dispersion if the unwoven fabric or unwoven fabric-shaped compound sheet contains

DMF-soluble fibers such as polyacrylonitrile as constituent fibers. Otherwise, PU is used as a DMF solution, and solidified by wet solidification using water or a mixture of water and DMF as the solidifying solution. The reason why this method is generally used is because the artificial leather obtained has a soft leather-like feel. The percentage of elastic polymer packed is 30% to 120% by weight of the fiber ingredients (extremely fine short fibers and any knit or weave) in the artificial leather produced. Preferably, 50% to 100% is more suitable for making the product leather-like. Packing too little elastic polymer gives a cotton-like feel, and packing too much gives a rubber-like feel, both of which are undesirable. Adding pigments such as carbon black to color elastic polymers is well-known, and pigments can also be added in this invention.

After packing with an elastic polymer, the PVA fibers are removed. The removal method may be to dissolve and remove PVA fibers by water at or above their solution temperature. PVA fibers may be extracted and removed in the same way when using sizing for starching or coating. So long as the sizing is water-soluble, it can be removed simultaneously with dissolving and removing PVA fibers.

A soft artificial leather is produced by the steps described above, but the surface may then be finished as desired, such as to a suede-like surface or silvered surface. Product quality can also be improved by other finishing such as brushing, embossing, applying an electrostatic finish, or applying a water repellant finish.

This invention was explained above following its production steps. This invention has the following characteristics:

- ① Extremely fine short fibers are used mixed with PVA fibers when producing an unwoven fabric comprised of extremely fine short fibers or an unwoven fabric-shaped compound sheet comprised of extremely fine short fibers and a knit or weave.
- ② The constituent fibers of said unwoven fabric or unwoven fabric-shaped compound sheet are confounded by spraying a high-speed water stream.
- ③ An elastic polymer is packed into the voids of said unwoven fabric or unwoven fabric-shaped compound sheet, then the PVA fibers are removed.

Results obtained as a result include the following:

- ① The extremely fine short fibers are easily confounded.
- ② The unwoven fabric or unwoven fabric-shaped compound sheet obtained by confounding the extremely fine short fibers by spraying a high-speed water stream is easily made high-density. Artificial leather obtained from this has high density and a hard paper-like feel, but artificial leather obtained by having PVA fibers present in an unwoven fabric or unwoven fabric-shaped compound sheet and removing these after packing with an elastic polymer has low density and can produce soft artificial leather with a leather-like feel. Softness can also be adjusted by varying

the amount of PVA fibers mixed in.

- ③ Using PVA fibers that are thicker than the extremely fine short fibers can lower the density of an unwoven fabric or unwoven fabric-shaped compound sheet obtained by confounding by spraying a high-speed water stream. Therefore, the artificial leather obtained has a soft feel, and because it is easily packed with an elastic polymer, an artificial leather with a leather-like feel is easily obtained.

Next, this invention will be explained in greater detail by giving working examples. Moreover, unless noted otherwise, "parts" and "%" in the working examples indicate parts by weight and per cent by weight. Weight was calculated by measuring the weight and the area, then dividing the weight by the area. Thickness was measured under a 20 g/cm² load, and apparent density was found by dividing the weight by the thickness, then correcting the units. Softness was measured by the 45° cantilever method.

Working Example 1

PET was spun using a conventional spinner, and 0.2 denier extremely fine fibers were produced by the super-draw method. These were cut to a length of 5 mm. These extremely fine short fibers mixed at different mixture ratios with a total of 100 parts PVA fibers that dissolve in 60°C or hotter water (1 denier, length: 6 mm) were dispersed in 50,000 parts room-temperature water to make paper-making slurries. The following substances were added to these slurries to

/520

facilitate dispersing fibers:

- polyacrylamide 17 ppm
- sodium 1-heptadecenyl-2-carboxyethoxyethylamidazoline 100 ppm
- hexamethylene glycol mono(nonylphenyl)ether 50 ppm
- nonionic defoaming agent 100 ppm

These slurries were subjected to paper-making to produce unwoven webs of 200 g/m² weight, and these were confounded by spraying a high-speed water stream to produce unwoven fabrics. The high-speed water stream was sprayed from 0.1 mm diameter columnar rectilinear nozzles at 25 kg/cm² pressure. The unwoven webs were set on 80-mesh wire screens having suctioning devices underneath, and struck by high-speed water streams from nozzles placed 30 mm apart. This operation was performed from both sides. Unwoven fabrics with different mixture ratios of extremely fine short fibers and PVA fibers were produced. The following table shows the compositions and physical properties of these.

Unwoven Fabric	A	B	C	D	E
PVA fibers / extremely fine short fibers	90 / 10	70 / 30	50 / 50	30 / 70	10 / 90
Weight	200 g/m ²	200	200	200	200
Thickness	0.97 mm	0.99	1.00	0.95	0.86
Apparent Density	0.21 g/cm ³	0.20	0.20	0.21	0.23

These unwoven fabrics were immersed in a 5% aqueous solution of PVA (Nippon Synthetic Chemical Industry, Gorsenol GL-05), confounded, then dried, leaving 13% PVA adhering to the unwoven fabrics. After starching, the unwoven fabrics were immersed in a 13% DMF solution of

a polyether type polyurethane elastomer, mixed by a mangle, then thrown into water to solidify the polyurethane (PU). Next, these were thrown into 90°C hot water to extract the PVA fibers and PVA, washed well with water, then dried. The following table shows the physical properties and feel of the artificial leathers obtained.

Unwoven Fabric	A	B	C	D	E
Weight (PU/fibers)	90 g/m ² (69/21)	130 (69/61)	175 (70/105)	208 (65/143)	232 (50/182)
Thickness	0.85 mm	0.87	0.90	0.87	0.80
Apparent Density (fiber components)	0.11 g/cm ³ (0.02)	0.15 (0.07)	0.19 (0.12)	0.24 (0.16)	0.29 (0.23)
Softness	35 mm	38	40	62	91
Feel	sponge-like	extremely soft leather-like, somewhat spongy rubber-like, lacks substantial feel	soft leather- like	leather- like to cotton- like	hard paper-like to cotton- like

Working Example 2

The following three types of unwoven webs were made by paper-making in the same way as in Working Example 1 using the same extremely fine short fibers and PVA fibers as Working Example 1.

Unwoven Web	A	B	C
PVA fibers / extremely fine short fibers	45 / 55	25 / 75	5 / 95
Weight	100 g/m ²	75	60

Two of these unwoven webs were laminated onto either side of a 50 g/m² weight tricot comprised of 75-denier/36-filament PET fibers, then confounded by spraying a high-speed water stream at 30 kg/cm² pressure in the same way as in Working Example 1 to produce unwoven fabric-shaped compound sheets. The following table shows the compositions and physical properties of these three types of unwoven

fabric-shaped compound sheets.

/521

Unwoven Fabric	A	B	C
Weight	250 g/m ²	200	170
Thickness	1.10 mm	0.81	0.60
Apparent Density	0.23 g/cm ³	0.25	0.28

10% PVA was adhered to these unwoven fabrics, then a 15% DMF solution of the same PU as in Working Example 1 was impregnated and solidified, and the PVA fibers and PVA were extracted and removed to produce artificial leathers. The following table shows the physical properties and feel of these artificial leathers.

Unwoven Fabric	A	B	C
Weight (PU/fibers)	269 g/m ² (106/163)	239 (73/166)	212 (44/168)
Thickness	1.02 mm	0.76	0.55
Apparent Density (fiber components)	0.25 g/cm ³ (0.16)	0.30 (0.22)	0.39 (0.31)
Softness	55 mm	60	95
Feel	soft leather-like	leather-like, somewhat hard cloth-like	cardboard-like

Working Example 3

The following three types of unwoven webs were made by paper-making in the same way as in Working Example 1 using the same extremely fine short fibers as Working Example 1 and the same PVA fibers as Working Example 1 except for making the fibers 3 mm long.

Unwoven Web	A	B	C
PVA fibers / extremely fine short fibers	45 / 55	65 / 35	85 / 15
Weight	75 g/m ²	115	265

These unwoven webs were used to produce unwoven fabric-shaped compound sheets by the same method as in Working Example 2. The

following table shows the compositions and physical properties of these three types of unwoven fabric-shaped compound sheets.

Unwoven Fabric	A	B	C
Weight	200 g/m ²	280	580
Thickness	0.80 mm	1.07	2.20
Apparent Density	0.25 g/cm ³	0.26	0.26

10% PVA was adhered to these unwoven fabrics, then a 15% DMF solution of the same PU as in Working Example 1 was impregnated and solidified, and the PVA fibers and PVA were extracted and removed to produce artificial leathers. The following table shows the physical properties and feel of these artificial leathers.

Unwoven Fabric	A	B	C
Weight (PU/fibers)	210 g/m ² (74/136)	239 (97/134)	326 (192/134)
Thickness	0.72 mm	0.96	1.90
Apparent Density (fiber components)	0.29 g/cm ³ (0.19)	0.24 (0.14)	0.17 (0.07)
Softness	42 mm	38	35
Feel	soft leather-like	extremely soft leather- like	extremely soft, but rubber-like and lacks substantial feel

Working Example 4

The following three types of unwoven webs were made by paper-making in the same way as in Working Example 1 using the same extremely fine short fibers as in Working Example 1 and 2-denier PVA /522 fibers 8 mm long.

Unwoven Web	A	B	C
PVA fibers / extremely fine short fibers	45 / 55	25 / 75	5 / 95
Weight	100 g/m ²	75	60

These unwoven webs were used to produce unwoven fabric-shaped compound sheets, then artificial leathers in exactly the same way as in Working Example 2. The following table shows the compositions and physical properties of these unwoven fabric-shaped compound sheets and artificial leathers.

Unwoven Fabric		A	B	C
Unwoven Fabric-Shaped Compound sheet	Weight	250 g/m ²	200	170
	Thickness	1.15 mm	0.85	0.68
	Apparent Density	0.22 g/cm ³	0.24	0.25
Artificial Leather	Weight (PU/fibers)	278 g/m ² (113/165)	246 g/m ² (80/166)	229 g/m ² (60/169)
	Thickness	1.08 mm	0.79	0.60
	Apparent Density (fiber components)	0.26 g/cm ³ (0.15)	0.31 (0.21)	0.38 (0.28)
	Softness	52 mm	58	96
	Feel	soft leather- like	leather-like, somewhat cotton-like	cardboard- like

Working Example 5

Thirty parts Nylon 6 extremely fine short fibers (0.3 denier, length: 8 mm) and 70 parts PVA fibers (2 denier, length: 8 mm) were dispersed in 50,000 parts water to make a paper-making slurry. This slurry was introduced to a 60 g/m² weight tricot comprised of 75-denier/36-filament Nylon 6 fibers inside the inlet of a paper-maker when making paper to produce a single three-layer laminated sheet having unwoven webs of 100 g/m² weight on both sides of a tricot. This laminated sheet was set on a net conveyor comprised of 80-mesh wire screen, and subjected to confounding treatment by a high-speed water stream while feeding at a speed of 1.5 m/min. Round holes of 0.2

diameter for rectilinear spraying were bored spaced at 1 mm to form a row lengthwise along a stainless pipe, and the outer wall of the part of the pipe bored with holes was shaved such that the round holes were 1.2 mm long. Both ends of the pipe were connected to a high-pressure pump, and the pipe was fixed at a position 25 mm above the net conveyor perpendicular to the feed direction of the net with the nozzles facing downward. A suction device was provided beneath the net conveyor so as to tightly adhere to the net. Another suction device the same as this was provided for treating both sides, enabling continuous confounding treatment on both the front and back. Water compressed to 10 kg/cm² by a high-pressure pump was sprayed from the nozzles, and an unwoven fabric-shaped compound sheet continuously confounded on both front and back was produced while removing the sprayed water by the suction devices. The unwoven fabric-shaped compound sheet obtained had 260 g/m² weight, 1.05 mm thickness, and 0.25 g/cm³ apparent density.

After adhering 10% PVA to this unwoven fabric-shaped compound sheet, this was buffed by #240 emery paper to smooth the surface, then immersed in a 15% DMF solution of the same PU used in Working Example 1. After confounding, the PU was solidified in water. However, the PU had 4% carbon black added to color it black. Next, the PVA fibers and PVA were dissolved and removed by hot water. The physical properties of the artificial leather obtained were 206 g/m² weight (PU/fibers: 96/110), 0.92 mm thickness, 0.22 g/cm³ apparent

density (fiber components: 0.12 g/cm^3), and 42 mm softness. It also had an extremely soft leather-like feel. Forming a 0.03 mm PU film on the front of this artificial leather produced soft artificial leather with a silvered surface. The PU film was formed by coating a DMF /523 solution of PU onto a release paper, tightly adhering this to the front of the artificial leather, and drying.

Working Example 6

Fifty parts PET extremely fine short fibers (0.2 denier, length: 5 mm) and 50 parts PVA fibers (4 denier, length: 12 mm) were dispersed in 50,000 parts water to make a paper-making slurry. This slurry was used to produce a three-layer laminated sheet in the same way as in Working Example 3. However, both of the unwoven web layers were of 120 g/m^2 weight, and a flat weave of 40 g/m^2 weight comprised of 75-denier/36-filament untwisted PET fibers was used as the knit or weave. The same apparatus as in Working Example 5 was used with the water pressure set to 12 kg/cm^2 when spraying with a high-speed water stream to make this laminated sheet an unwoven fabric-shaped compound sheet. The unwoven fabric-shaped compound sheet obtained had 280 g/m^2 weight, 1.33 mm thickness, and 0.21 g/cm^3 apparent density.

After shaving 0.05 mm of the front and 0.10 mm of the back of this unwoven fabric-shaped compound sheet using #240 emery paper, 13% PVA was adhered. Next, an 18% solution of CMC (Dai-ichi Kogyo Seiyaku, Fine Gum SP-1) was coated onto the front by a doctor knife, then dried. The amount of CMC coated was 35 g/m^2 . The black PU used in

Working Example 5 was impregnated into this unwoven fabric-shaped compound sheet, then solidified. Next, the PVA fibers, PVA, and CMC were dissolved and removed in hot water. The artificial leather obtained had 245 g/m² weight (PU/fibers: 102/143), 1.04 mm thickness, 0.24 g/cm³ apparent density (fiber components: 0.14 g/cm³), and 53 mm softness.

Working Example 7

Seventy parts PET extremely fine short fibers (0.1 denier, length: 5 mm) and 30 parts PVA fibers (1 denier, length: 6 mm) were dispersed in 50,000 parts water to make a paper-making slurry. This slurry was used to produce a three-layer laminated sheet in the same way as in Working Example 3. However, both of the unwoven web layers were of 100 g/m² weight, and the flat weave used in Working Example 6 was used as the knit or weave. This three-layer laminated sheet was sprayed by a rectilinear water stream from both the front and back in the same way as in Working Example 5 to make an unwoven fabric-shaped compound sheet. However, water-spray nozzles having 0.2 mm diameter round holes were attached to a stainless steel pipe as the spraying apparatus. Fifteen stainless steel pipes with nozzles attached at 15 mm intervals were arranged offset by 1 mm such that the nozzle positions overlapped across the width. This compound spraying apparatus revolved in a 10-mm circle within the same plane. The speed of one revolution was 160 min. Confounding treatment was performed by spraying water at 15 kg/cm² water pressure at a net speed of 1.5 m/min

to produce an unwoven fabric-shaped compound sheet. The unwoven fabric-shaped compound sheet had 240 g/m² weight, 1.03 mm thickness, and 0.23 g/cm³ apparent density.

After shaving 0.05 mm of the front and 0.10 mm of the back of this unwoven fabric-shaped compound sheet using #240 emery paper, 13% PVA was adhered. A 34% solution of PVA was coated onto the front. Next, this was starched by coating 13% PVA, and a 34% aqueous solution of PVA was coated onto the front. The amount of PVA coated was 30 g/m². The black PU used in Working Example 5 was impregnated into this unwoven fabric-shaped compound sheet, then solidified. Next, the PVA fibers and PVA were dissolved and removed in hot water. The artificial leather obtained had 238 g/m² weight (PU/fibers: 80/158), 0.80 mm thickness, 0.31 g/cm³ apparent density (fiber components: 0.20 g/cm³), and 60 mm softness. Although somewhat deficient in softness and leather-like feel, it had a large amount of napping and a fine suede-like surface.

Working Example 8

Seventy parts PET extremely fine short fibers (0.1 denier, length: 5 mm) and 30 parts PVA fibers (1 denier, length: 6 mm) were dispersed in 50,000 parts water to make paper-making slurry (I). Separately from this, 20 parts of the same extremely fine short fibers and 80 parts of the same PVA fibers were dispersed in 50,000 parts water to make paper-making slurry (II). Slurries (I) and (II) were separately fed to each inlet of a paper-maker with two inlets,

and the same flat weave as used in Working Example 6 was introduced between the two inlets to produce a three-layer laminated sheet. The upper-layer unwoven web of the three-layer sheet had a 70:30 mixture ratio of extremely fine short fibers to PVA fibers and 100 g/m² weight, and the lower-layer unwoven web of the three-layer sheet had a 20:80 mixture ratio of extremely fine short fibers to PVA fibers and 100 g/m² weight. This three-layer sheet was sprayed by a high-speed water stream to make an unwoven fabric-shaped compound sheet in the same way as in Working Example 7. The unwoven fabric-shaped compound sheet had 240 g/m² weight, 1.08 mm thickness, and 0.22 g/cm³ apparent density. /524

This unwoven fabric-shaped compound sheet was buffed, starched, coated with PVA, and impregnated with PU, then the PU was solidified and the PVA fibers and PVA was dissolved and removed in the same way as in Working Example 7. However, the surface layer had a 70:30 mixture ratio of extremely fine short fibers to PVA fibers. The artificial leather obtained had 198 g/m² weight (PU/fibers: 84/114), 0.84 mm thickness, 0.24 g/cm³ apparent density (fiber components: 0.14 g/cm³), and 42 mm softness, and was a suburb suede-finished artificial leather with a supple leather-like feel and fine suede-like surface.

Working Example 9

A three-layer sheet was made by paper-making using the same extremely fine short fibers, PVA fibers, and flat weave and by the same method as in Working Example 8. The weight of both layers of

unwoven webs was 100 g/m², but the mixture ratio of extremely fine short fibers to PVA fibers was 95:5 in the unwoven web on the front and 5:95 in the unwoven web on the back. This three-layer sheet was sprayed with a high-speed water stream to make an unwoven fabric-shaped compound sheet in the same way as in Working Example 7. The unwoven fabric-shaped compound sheet had 240 g/m² weight, 1.05 mm thickness, and 0.23 g/cm³ apparent density.

This unwoven fabric-shaped compound sheet was buffed, starched, coated with PVA, and impregnated with PU, then the PU was solidified and the PVA fibers and PVA was dissolved and removed in the same way as in Working Example 7. The artificial leather obtained had 202 g/m² weight (PU/fibers: 81/121), 0.81 mm thickness, 0.15 g/cm³ apparent density (fiber components: 0.14 g/cm³), and 48 mm softness, and was a suede-finished artificial leather with a soft leather-like feel and fine suede-like surface.

Working Example 10

Sixty parts 0.1 denier 3-mm long polyacrylonitrile fibers and 40 parts 1 denier 3-mm long PVA fibers length were dispersed in 50,000 parts water to make a paper-making slurry. This was subjected to paper-making on a knit ground of 90 g/m² weight comprised of 150-denier/72-filament PET fibers by the same method as in Working Example 5 to produce a two-layer sheet of 180 g/m² weight. This was confounded on a 120-mesh wire screen using the spraying apparatus in Working Example 5 to produce an unwoven fabric-shaped compound sheet.

However, confounding treatment was performed by spraying water at 15 kg/cm² water pressure from the unwoven web side. The unwoven fabric-shaped compound sheet obtained had 180 g/m² weight, 0.82 mm thickness, and 0.22 g/cm³ apparent density.

This unwoven fabric-shaped compound sheet was subjected to napping treatment using #150 emery paper, an acrylic sizing insoluble in water (Tagai Okagaku Plastic Sizing 208C) was coated and dried on this napped surface, then an aqueous emulsion of PU was impregnated and dried. Next, the PVA fibers and the acrylic sizing were extracted by heating in a sodium bicarbonate aqueous solution to produce an artificial leather. The artificial leather obtained had 211 g/m² weight (PU/fibers: 72/139), 0.71 mm thickness, 0.30 g/cm³ apparent density (fiber components: 0.20 g/cm³), and 51 mm softness, and was a suede-finished artificial leather having a suede-like finish with a soft feel.